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THE GOTO LABORATORY

Head: Prof. Dr. Rempei Goto

In 1947 Prof. Rempei Goto succeeded Prof. S. Horiba as head of the laboratory of physical chemistry in the Institute for Chemical Research. Main subjects of research in this laboratory are colloid chemistry and non-stationary reaction as inflammation or explosion. Chief results obtained during these five years are reviewed below.

I. Explosion and Inflammation

1. Dust Explosion. R. Goto and E. Suito¹⁾ inflamed aluminium smoke blown out through a narrow tube with a flame of coal gas which was placed at various distances (d) from the exit of the tube. Limiting curves of inflammability were obtained as a relation between d and a , the critical quantity of the powder. The relation was given by

$$\log a = K + n \log d$$

where K is an inflammability constant and n a spreading constant. R. Goto, E. Suito and K. Taki²⁾ confirmed that this relation holds good for various kinds of organic powders as well as coal dusts. They investigated the effect of various additional³⁾, and found that most of additional besides some oxidizing agents shows a retarding effect. It was found that the inflammation of coal dust can be remarkably suppressed by ultra-fine or colloidal powder of CaCO_3 and that then the coal particles are enveloped by colloidal powder.

2. A Monistic Theory of Explosion Limit and Propagation Velocity. R. Goto⁴⁾ had claimed that the limiting properties and propagating character were essential to explosive reaction; thereupon he and N. Hirai⁵⁾ proposed a monistic theory from which the limiting condition and velocity of detonation wave can be derived.

The temperature relation of the lower limit of concentration (C) were given by

$$C \cdot Q/F + 1/2 \cdot RT = \varepsilon \quad \dots\dots\dots(1)$$

where Q is the heat of reaction, F the total freedoms of molecules of reaction products, R the gas constant, T the absolute temperature of the experiment and ε the energy of activation.

From (1), the energy of activation could be estimated and was shown to take approximately the same value (about 2 Kcal.) for most of the combustible gases.

The propagation velocity of detonation \bar{V}_d was given by the relation

$$1/2 \cdot M \bar{V}_d^2 = JQ \cdot f_t/F - 1/2 \cdot RT \quad \dots\dots\dots(2)$$

where M is the total mass of reaction products, J the mechanical equivalent of heat, f_t the freedoms of translation, F total freedoms of molecules of the reaction products. The calculated values agreed with the experimental results of many

detonating gases. Further, the detonation velocities of solid explosives \bar{V}_s were given by

$$\bar{V}_s = \bar{V}_g (v/v_f)^{1/3} \quad \dots\dots\dots(3)$$

where \bar{V}_g is the propagation velocity defined by the relation (2), v the molecular volume and v_f the free volume of the explosives. It was shown that calculated velocities of many explosives, which belong to molecular crystal, agreed with the experimental values.

- 1) R. Goto and E. Suito: Rev. Phys. Chem. Japan, Commemoration Volume, p. 82 (1946).
- 2) R. Goto, E. Suito and K. Taki: Science of Powder (Japan), **2**, 87 (1948).
- 3) R. Goto, E. Suito and K. Taki: J. Ind. Expl. Soc. Japan, **11**, 44 (1950).
- 4) R. Goto: Rev. phys. Chem. Japan, **16** 152 (1942).
- 5) R. Goto: Bul. Inst. for Chem. Res., Kyoto Univ., **21**, 1 (1950).
- 6) R. Goto and N. Hirai: Bul. Inst. for Chem. Res., Kyoto Univ., **23**, 28 (1950).

II. Dispersoid Analysis

Various methods of the determination of particle size and size distribution of powders in subsieved range were investigated.

E. Suito and M. Arakawa¹⁾ invented an automatic recording sedimentation balance as a simple and precise apparatus of the sedimentation method to determine the distribution curve of particle size between 40μ and 0.5μ ; and this new instrument "Sedimentographer" is in demand from Shimadzu Co. As the old automatic apparatus for balance method are too complicated, they have devised an improved apparatus, quite new and of very simple mechanism for general industrial use. By means of this apparatus, they examined the fundamental problems of sedimentometry, especially the effect of peptizer, temperature and the concentration of suspension. They also studied on the condition of sedimentometry for many samples applicable for practical use--inorganic pigments, fillers for rubber and paper, portland cements, metal powders, battery materials, natural soil, etc.

E. Suito and N. Hirai²⁾ proposed a new idea that the particle sized distribution can be obtained by measuring reaction velocity. Now we assume a system of n particles with radius r , the mass of a particle m , total mass M , the surface area of a particle s and total surface area S , then

$$M = nm = \frac{3}{4}\pi n \rho r^3 \quad (\rho: \text{density})$$

$$S = ns = 4\pi nr^2$$

$$\therefore S = an^{1/3} M^{2/3}, \quad a = 4\pi \left(\frac{3}{4}\pi \rho \right)^{-2/3}$$

As the reaction velocity is proportional to the surface area and the concentration $[C]$ of the solution of reactant,

$$-\frac{dM}{dt} = kS[C]$$

Under the condition of $[C] = \text{const.}$, if the particles are dissolved completely,

namely $M=0$, then time t becomes,

$$\tau = br., \quad b = \frac{3}{k} \left(\frac{4}{3} - \pi \rho \right)^{1/3}$$

And

$$M = n \frac{k^3}{27} (\tau - t)^3$$

$$\therefore \frac{d^2M}{dt^2} = n \frac{2}{9} k^3 (\tau - t).$$

The relation between the variation of reaction velocity with time $-\frac{d^2M}{dt^2}$ and the time t is linear, and the intersection of the line to time axis τ is propotional to the radius of particles r_0 and the inclination to particle number n . In the hetro-disperse system of powders of various radius, a curve composed of the sum of the straight lines above-mentioned which correspond to each particle size is obtained. From the analysis of this curve similar to the sedimentation method, the distribution curve of particle size is obtained. As an example, E. Suito and K. Taki²⁾ measured the size distribution of calcium carbonate powders from its dissolving velocity to acetic acid by the method of thermal analysis of reaction velocity, and the distribution curves coincided which were obtained by other methods. Out of the mixed powder of calcium carbonate and titanium oxide, only the distribution curve of the former was obtained. This method can be applied to measuring over a wide range of size distributions from colloidal dimension to sieve.

E. Suito, M. Arakawa and T. Okumura³⁾ measured the mean radius, or specific surface area of various powders by the adsorption method in the liquid phase. The adsorbents were stearic acid, palmitic acid, oleic acid, methyl stearate, glycohol distearate, etc., and the solvents were benzene toluene and carbon tetrachloride. Similar to the gas phase, the B.E.T. relation hold good, and the volume of adsorbent necessary to form a monolayer V_m and the difference of the heat of adsorption and liquefaction $\Delta E = E_a - E_c$ was calculated. They also carried out experiments on various types of the permeability method.

- 1) E. Suito and M. Arakawa: Bull. Inst. for Chem. Res., Kyoto Univ., **19**, 43 (1949), *ibid*, **22**, 7 (1950).
- 2) E. Suito, N. Hirai and K. Taki: *Ibid*, **22**, 81 (1950), J. Chem. Soc. Japan., **72**, 713 (1951).
- 3) E. Suito, M. Arakawa and T. Okumura: Meeting on the Discussion of Colloid Chemistry held by Chem. Soc. Japan, 19, Nov (1950).

III. Morphology of Colloidal Systems (Electron Microscopy and Electron Diffraction of Colloidal Particles and Ultrafine Powders)

E. Suito, N. Uyeda, M. Arakawa and I. Takiyama are investigating on the colloidal particles and ultrafine powders by means of electron microscopy and electron diffraction (a new SMT 4 type).

Electron microscopy of the colloidal particles of gold sol¹⁾ which was formed by various methods--Zsigmondy's, Weimarn's, Farady's and reduction by hydrogen

peroxide, hydrazine, gas etc.—was obtained, and the relation between the particle size and the colour of sol was discussed. Especially, the sols prepared by the reduction method of hydrogen peroxide were examined in a wide range of pH of starting solution. Trigonal and hexagonal particles were found, and they were considered to have grown to large thin plates. It was proved by electron diffraction patterns that those very thin plates are gold crystal, having trigonal and hexagonal surfaces largely grown up along the (111) plane.

Electron micrograph of mercury emulsion²⁾ was observed as a new departure to observe ultrafine liquid drops. This emulsion was made in collodion solution by ultrasonic wave and was bedded in its membrane. Both the large particle $1\sim3\mu$ and small $10\sim100m\mu$ in diameter were round at first, but the latter aggregated to an arabesque structure.

Taking electron micrograph of a few kind of organic pigments,³⁾ known as Sherdye and Aridye used for Pigment Regain Printing, such items as the shape of the particles, the particle size distribution, the state of aggregation and the influence of ultrasonic wave on the aspect of dispersion were studied. The process of the recrystallization was studied by electron diffraction.

Various kinds of ultrafine powders for industrial use, common goods and many samples made in our laboratory, was investigated by electron microscopy and electron diffraction to estimate the correlation between the quality of powders and those items, the size, the shape and the size distribution.⁴⁾

- 1) E. Suito, N. Uyeda and M. Arakawa: Meetings on the Discussion of Colloid Chemistry held by Chem. Soc. Japan, 18. Nov (1950). Report of Committee on Electron Microscopy, 56-C-17. 57-C-1, Kagaku **21**, 598 (1951).
- 2) E. Suito and N. Uyeda: Report of Committee on Electron Microscopy, 56-C-9 (1951).
- 3) E. Suito and N. Uyeda: Meeting of Chem. Soc. Japan, 19, May (1951).
- 4) E. Suito, M. Arakawa and N. Uyeda: Bull. Inst. Chem. Rev., Kyoto Univ. **24**, 74 (1951).

IV. Rheological Properties of Colloidal Systems and Solvation

1. Viscosity of Non-ionic Detergent Solution and its Molecular Weight.

R. Goto, N. Koizumi and T. Sugano¹⁾ studied viscosity measurements of non-ionic detergents solution such as $H(OCH_2CH_2)_M O(CH_2)_N H$ in organic solvents, and found that the intrinsic viscosity $[\eta]$ can be given generally by the relation

$$[\eta] = A[M]^a + B[N]^b + C$$

where A, B, C, a and β are certain constants, respectively. Degrees of solvation in various solvents were discussed.

2. Plastic Deformation and Slip Bands.

R. Goto and N. Hirai²⁾ found that when a block of bentonite clay kneaded with water were pressed with two parallel planes, there appeared distinct slip bands on the surface of the clay and the bands were inclined at 45° in the direction of the force applied. The slip bands changed their appearance after heat treatment or giving certain additional such as NaCl or alcohol. Using organic liquid instead of water, slip bands disappeared but lines of

crevice appeared which was inclined at 30° in the direction of the force. These lines of crevice were observed for most of the systems which show dilatancy. It was suggested that such slip bands or lines of crevice are closely related to the degree of solvation of solid particles.

3. Swelling of Bentonite. S. Ono and T. Watanabe³⁾ examined the swelling behaviour of bentonite treated under various temperatures and pressures. Generally, swelling of bentonite dehydrated under high temperature was markedly reduced, but could be recovered by autocraving as well as by the irradiation of ultrasonic waves. The swelling capacity was attributed to the existence of some parts in the structure of bentonite where dehydration takes place in the two temperature ranges 450° – 800°C and 180°C . It was suggested that the former determines whether the bentonite exhibits the swelling or not.

- 1). R. Goto, N. Koizumi and T. Sugano: Bull. Inst. Chem. Res. Kyoto Univ., (1951) in press.
- 2) R. Goto and N. Hirai: *Ibid.*, **20**, 48 (1950).
- 3) S. Ono and T. Watanabe: *Ibid.*, **17**, 101 (1949); **13**, 112 (1949); J. Chem. Soc. Japan, 71, 574, 631 (1950).

V. Dielectric Investigation of Colloidal Systems

1. Emulsion. R. Goto and N. Koizumi¹⁾ measured the dielectric constants of emulsions of the type, oil-in-water or water-in oil, at the frequency of 214 MC. It was found that for the oil-in water type emulsion Bruggeman's equation holds but for the water-in-oil type emulsion the equation does not hold. Against expectation, the water-in-oil type emulsion showed remarkable absorption, and it was attributed to the presence of ionic emulsifier in the water.

2. Starch and its Water Content. S. Ono, K. Koizumi and T. Kuge²⁾ examined the nature of water absorbed by starch by measuring its dielectric properties. The samples were suspended in liquid paraffin, and the water content of the starch was varied. The dielectric constant ϵ' and loss ϵ'' were measured at the frequency of 214 MC and various frequencies between 3 and 30 MC, the temperature being varied from 10 to 55°C . ϵ' rises with increasing temperature and content of water. ϵ'' has the maximum at a certain temperature and frequency. This loss was attributed to the rotation of dipoles of water molecules in starch. The relaxation time was evaluated from the results and it was found that the more the moisture content the smaller becomes the relaxation time. Those results were discussed from the standpoint of the theory of absolute reaction rate.

3. Dielectric Measurements at Microwave Frequencies. N. Koizumi³⁾ designed and constructed an experimental equipment for measuring the complex dielectric constant ϵ^* at microwave frequencies. It operates at the wavelength range of 8–12 cm and consisted of several waveguide components. As the signal generator, a reentrant cavity oscillator using a light house tube (2C40), was employed. The dielectric properties of solid samples were calculated from the observed voltage standing wave ratio and the location of the voltage minimum point for a short-

circuit and an open-circuit termination. The dielectric constant and loss tangent ($\tan \delta$) of some solid samples were measured by this method.

- 1) R. Goto and N. Koizumi: Bull. Inst for Chem. Res., Kyoto Univ., **18**, 121 (1949).
- 2) S. Ono, N. Koizumi and T. Kuge: *Ibid.*, **20**, 46 (1950); **21**, 80 (1950).
- 3) N. Koizumi: *Ibid.*, **25** (1951), in press.

VI. Organic Colloid Chemistry and its Application

1. Organosol. As a serial of the studies on organosols, prepared by the metal organosol formation method, the investigation on mercury organosol was made by I. Yamakita and coworker.

In the case of mercury organosol,¹⁾ any dispersion medium, having the faculty to form so stable sol as gold and silver organosols, was not found. Some properties of mercury organosol (particle size, viscosity etc.) were examined. The results obtained were discussed in comparison with those in the case of gold and silver organosols.

2. Oil Refining. The purification of rice oil was one of the most important problems in oil industry. Although much work on this subject was done, no satisfactory solution was obtained. I. Yamakita made studies²⁾ on the purification of dewaxed rice oil from the colloid chemical standpoint. From the results obtained the following conclusion was derived. Crude dewaxed rice oil contains such impurities as intense coloring matters originated from oil soluble iron compounds and other surface active substances beside normal components of oil. These impurities can be accumulated at the oil-water interface, if the crude oil is emulsified with dilute aqueous solution of strong acids or some salts (for ex. natrium citrate, magnesium chloride etc.) and deemulsification occurs naturally. Thus the purification of crude dewaxed rice oil can be done without difficulty as well as in the case of other vegetable oils. This method for the purification of rice oil was tested on a semi-commercial scale in the Goto Laboratory.³⁾

3. Oil Polymerisation. A study on the thermal polymerisation of high acid value rice oil was made by I. Yamakita and S. Tomioka. It was found that the polymerisation process was promoted most remarkably by the addition of 1% magnesia or litharge to the oil. The separation of non-drying component from oil was tried by the vacuum distillation of the intensively polymerized oil, and this attempt was successful as was expected. This method of procedure for high acid value rice oil was registered as a Japanese patent.⁴⁾

4. The Hydrogenation of Oil. E. Suito and H. Aida⁵⁾ studied kinetically the hydrogenation of oleic acid and methyl oleate, an example of the simplest fatty acid, by the method of thermal analysis of reaction velocity in liquid phase. The temperature of the reaction was 80, 100, 120 and 140°C, oleic acid and methyl oleate 29.9 or 49.6 g, Raney Ni catalysts 0.3~1.5 g, flow rate of hydrogen 200, 400 and 600 cc/min. Hydrogenation was the first order reaction, and the velocity constants were small. Also the rate of reaction was proportional to the quantity of catalysts

and the flow rate of hydrogen. The value of activation energy was 8.3 Kcal in the case of oleic acid and 5.8 Kcal methyl oleate. The heat of hydrogenation was evaluated as 37.2 Kcal/mol in both cases.

5. Ship Bottom Paints. S. Shimomoto made tests on manufacturing of ship bottom paints on a semi-commercial scale in the Goto Laboratory, using patented methods. Furthermore, he tried to use rice oil as one of the raw materials of paints, and this attempt seems to be hopeful.

- 1) I. Yamakita and F. Takenaka; Bull. Inst. for Chem. Res., Kyoto Univ., **22**, 89 (1950).
- 2) I. Yamakita: *Ibid.*, **24**, 24 (1951).
- 3) I. Yamakita and coworkers: *Ibid.*, **24**, 82 (1951).
- 4) S. Shimomoto and I. Yamakita: Japanese patent. No. 187189.
- 5) E. Suito and H. Aida: J. Chem. Soc. Japan (Ind. Chem. Section), **72** (1951) in press